Original Article

Effect of iron content on $\beta \to \alpha$ phase transformation behavior of Ti-5Al-xFe ($x=1, 2.5, 4$) alloys during continuous cooling

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ABSTRACT
We investigated the effect of Fe content on the $\beta \to \alpha$ phase transformation behavior of Ti-5Al-xFe ($x=1, 2.5, 4$) alloys during continuous cooling. The presence of Fe delayed long-range diffusional phase transformation, thus facilitating diffusionless transformation even at low cooling rates. This effect was explained by the extremely low solubility of Fe atoms in the $\alpha$ phase, so that they must be significantly redistributed before the precipitation of the equilibrium $\alpha$ phase. Fe also reduced the phase-transformation start temperature by lowering the $\beta$-transus temperature. Differences in the $\beta$-transus temperature of the alloys accounted for the differences in the phase-transformation start temperature at a low cooling rate. However, as the cooling rate increased, the difference in the phase-transformation start temperature greatly increased, which could no longer be explained by the difference in the $\beta$-transus temperature. It was reasoned that Fe significantly stabilized the $\beta$ phase; hence, the effective $\beta$-transus temperature decreased as the cooling rate increased. This reduction was intensified by an increase in the Fe content. The strong dependence of the $\beta \to \alpha$ phase transformation behavior on the Fe content led to the development of different microstructures in the alloys. Hardness was strongly dependent on the resulting microstructure, which differed with the Fe content and cooling rate. Our results provide a clear understanding of the $\beta \to \alpha$ phase transformation behavior of these alloys and would be useful for designing appropriate solution heat treatment.

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1. Introduction
Titanium alloys undergo a $\beta \to \alpha$ phase transformation during continuous cooling from the $\beta$-phase field. The resulting microstructure relies on the following transformation mechanisms [1]. Diffusionless transformations are observed at high cooling rates, wherein a phase change occurs by cooperative atom shuffling across a habit plane without atomic diffusion [2,3], yielding a martensitic structure. Diffusional transformations occur at low cooling rates, wherein the phase transformation is caused by long-range diffusion of atoms.
in an equilibrium manner [2]. Diffusional $\beta \rightarrow \alpha$ transformations typically lead to the development of Widmanstätten and lamellar structures [4,5]. Understanding both the $\beta \rightarrow \alpha$ phase transformation behavior and resultant microstructures is important, as the mechanical properties of Ti alloys are intrinsically linked to the microstructure. Hence, control of the microstructure can lead to improved mechanical properties.

The Ti-6Al-4V alloy is frequently used in industrial fields, and thus, its phase transformation behavior during continuous cooling has been intensively researched [6-11]. Rapid cooling (>410°C/s) from the $\beta$ region leads to martensite formation in this alloy [6]. However, at more moderate cooling rates (20-410°C/s), a Widmanstätten structure with very thin $\alpha$ plates develops [6], whereas at low cooling rates (1.5°C/s), a coarse lamellar structure is formed [8-11]. These reports show that the cooling rate strongly influences the $\beta \rightarrow \alpha$ phase transformation behavior. Such well-established knowledge of the phase transformation behavior of this commercial Ti alloy has provided important guidelines for designing suitable heat treatments to tailor the microstructure and hence control the mechanical properties of the alloy.

The phase transformation behavior of Ti alloys is also affected by their chemical composition [12-14], as the difference in diffusivities among the alloying elements leads to differences in the phase transformation kinetics [15,16]. In addition, $\beta$-stabilizing alloying elements can affect the overall phase transformation behavior, because they tend to retain the $\beta$ phase even below the $\beta$-transus temperature, $T_{\beta}$ [17,18]. Thus, the phase transformation behavior of any newly developed Ti alloy must be clarified.

Recently, the Ti-Al-Fe system has been evaluated as an alternative to the Ti-6Al-4V alloy for the following reasons: (1) Fe is less expensive than V and imparts a lower processing temperature, thus reducing the manufacturing cost [19]; (2) the mechanical properties of the Ti-Al-Fe system are comparable to those of Ti-6Al-4V [20]. However, the phase transformation behavior of Ti-Al-Fe alloy during continuous cooling is not well understood. In addition, Fe is a strong $\beta$ stabilizer, so the effects of Fe content on the phase transformation behaviour should be determined.

In the present study, we evaluated the $\beta \rightarrow \alpha$ transformation behavior of Ti-5Al-xFe ($x = 1, 2.5, 4$) alloys during continuous cooling at rates of 0.01-75°C/s to clarify the influence of Fe on the phase transformation and resultant microstructure. We also measured the Vickers hardness of the alloys to examine how the transformation mechanism and microstructure affect the material strength of these alloys.

## 2. Materials and methods

Ingot of Ti-5Al-xFe ($x = 1, 2.5, 4$) alloys were produced by induction skull melting [21]. The raw materials had high purities (>99.9%) and were supplied by iTASCO. The chemical compositions (Table 1) of the ingots were measured using an inductively coupled plasma-optical emission spectrometer (ICAP6500, Thermo Electron) and an N/O/H determinator (ONH836, LECO). To break up their large columnar casting structures, the ingots were forged first at 1070°C in the $\beta$-phase field and then at 770°C in the $(\alpha + \beta)$-phase field.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Al</th>
<th>Fe</th>
<th>N</th>
<th>O</th>
<th>H</th>
<th>Ti</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-Fe</td>
<td>4.80</td>
<td>1.06</td>
<td>0.006</td>
<td>0.068</td>
<td>0.006</td>
<td>Bal.</td>
</tr>
<tr>
<td>2.5-Fe</td>
<td>4.82</td>
<td>2.49</td>
<td>0.006</td>
<td>0.064</td>
<td>0.006</td>
<td>Bal.</td>
</tr>
<tr>
<td>4-Fe</td>
<td>4.80</td>
<td>3.87</td>
<td>0.005</td>
<td>0.055</td>
<td>0.006</td>
<td>Bal.</td>
</tr>
</tbody>
</table>

The forged alloys were annealed at 800°C for 2h; all the annealed alloys had a well-forged microstructure comprising equiaxed $\alpha$-phase grains with a size of 30-64 μm. The resulting specimens were used to examine the phase transformation. Hereafter, the Ti-5Al-1Fe, Ti-5Al-2.5Fe, and Ti-5Al-4Fe alloys will be denoted as 1-Fe, 2.5-Fe, and 4-Fe, respectively.

Simultaneous thermogravimetric analysis/differential scanning calorimetry (TGA/DSC; Q-600, TA Instrument) was used to measure the $T_{\beta}$ value of the three alloys. For this measurement, the change in the heat flux per unit weight was monitored as the temperature was increased at 1200°C at a rate of 5°C/min. The $T_{\beta}$ values for the 1-Fe, 2.5-Fe, and 4-Fe samples were 990, 959, and 923°C, respectively (Fig. 1).

To monitor the $\beta \rightarrow \alpha$ transformation during continuous cooling, a dilatometer test (Dilatronic-III, Theta) was performed under vacuum ($3.0 \times 10^{-4}$ Torr). For this purpose, the samples were machined into rods with a diameter of 3 mm and a length of 10 mm. The length change of the rods was measured during cooling from 1070°C in a $\beta$ single-phase field. Seven cooling rates (75, 20, 7.5, 3, 1, 0.3, and 0.1°C/s) were used in this test.

The microstructures of the samples were examined using optical microscopy (OM; GX51, OLYMPUS) and electron backscatter diffraction (EBSD; NordlysNano, Oxford) at an acceleration voltage of 15 kV and a step size of 50nm. For the OM observations, the sample surface was mechanically polished, electropolished, and finally etched using Kroll’s reagent (5 ml HNO3, 10 ml HF, and 85 ml distilled H2O). Surfaces were electropolished using a LectroPol-5 apparatus at a voltage of 22 V for 22 s in a solution of 410 ml methanol, 245 ml 2-butoxyethanol, and 40 ml HClO4. For EBSD measurements, the sample surface was mechanically polished and electropolished as mentioned above. The chemical composition of the phases was measured by energy-dispersive spectroscopy (EDS, X-MaxN, Oxford Instruments) mounted in a scanning electron microscope (SEM, JSM-7001F, JEOL) operating at an accelerating voltage of 20 kV. The sample for this measurement was prepared in the same way as that used for the OM observations.

To examine the nanosized phase precipitation, transmission electron microscopy (TEM; JEM 2100F, JEOL) was performed at an accelerating voltage of 200 kV. TEM samples were prepared by twin-jet electropolishing (Tenupol-5, STRUERS) in a solution of 100 ml HClO4 and 900 ml CH3OH. The hardness was evaluated using a micro-Vickers tester (FM-700, Future-Tech).

## 3. Results

### 3.1 Continuous cooling phase transformation

The $\beta \rightarrow \alpha$ transformation yields two inflection points in the dilatometer measurements of reduction in sample length
during cooling (Fig. 2). The high-temperature and low-temperature inflection points correspond to the beginning and end of the phase transformation, respectively. These temperatures, denoted as the transformation start temperature, \( T_s \), and transformation finish temperature, \( T_f \), respectively, were affected by cooling rate in each of the alloys tested (Table 2). This phenomenon was used to examine the effect of the cooling rate on the phase transformation behavior of the alloys. In 1-Fe, the phase transformation was initiated at 807 °C during cooling at the highest cooling rate of 75 °C/s. This increased to 958 °C as the cooling rate was decreased to 0.1 °C/s (Fig. 2a; Table 2). This variation in \( T_s \) is related to a change in the dominant phase transformation mechanism [2], as confirmed by microstructural observations (Fig. 3a). A typical martensitic structure was observed at high cooling rates of 75 and 20 °C/s (Fig. 3a), verifying that the phase transformation occurred mainly via the diffusionless mechanism at cooling rates \( \geq 20 \) °C/s. Cooling at 7.5 °C/s generated a microstructure comprising the Widmanstätten structure and \( \alpha \) layers along the prior \( \beta \) grain boundaries, both of which are caused by diffusional transformation [4,5]. At cooling rate of \(< 7.5 \) °C/s, a

Table 2 – Start and end temperatures of \( \beta \rightarrow \alpha \) phase transformation.

<table>
<thead>
<tr>
<th>Cooling rate [°C/s]</th>
<th>1-Fe alloy</th>
<th>2.5-Fe alloy</th>
<th>4-Fe alloy</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Start</td>
<td>Finish</td>
<td>Start</td>
</tr>
<tr>
<td>0.1</td>
<td>958</td>
<td>693</td>
<td>960</td>
</tr>
<tr>
<td>0.3</td>
<td>949</td>
<td>716</td>
<td>899</td>
</tr>
<tr>
<td>1</td>
<td>920</td>
<td>701</td>
<td>901</td>
</tr>
<tr>
<td>3</td>
<td>902</td>
<td>720</td>
<td>820</td>
</tr>
<tr>
<td>7.5</td>
<td>866</td>
<td>680</td>
<td>794</td>
</tr>
<tr>
<td>20</td>
<td>817</td>
<td>676</td>
<td>781</td>
</tr>
<tr>
<td>75</td>
<td>807</td>
<td>711</td>
<td>750</td>
</tr>
</tbody>
</table>
Fig. 3 – OM images of the three alloys continuously cooled at 75 °C/s: (a) 1-Fe, (b) 2.5-Fe, and (c) 4-Fe; ‘, martensitic structure; α_{GB}, α phase nucleated at prior β grain boundaries; α_{W}, Widmanstätten structure; α_{L}, lamellar structure.
lamellar structure with coarsening α plates developed, indicating that diffusional transformation was dominant.

2.5-Fe and 4-Fe also underwent diffusionless β → α transformation at high cooling rates and diffusional transformation at low cooling rates (Figs. 2 and 3). However, the cooling rates at which these two transformation mechanisms were transposed were different for the three alloys. The martensitic structure disappeared almost completely from the microstructure at cooling rates of <7.5 °C/s in 1-Fe (Fig. 3a), <3 °C/s in 2.5-Fe (Fig. 3b), and <1 °C/s in 4-Fe (Fig. 3c). Similarly, the Widmanstätten structure was observed in the microstructure at a lower cooling rates as the Fe content increased: 7.5 °C/s in 1-Fe and 3 °C/s in 4-Fe. Furthermore, the average thickness of the α plates in the lamellar structure at a cooling rate of 0.01 °C/s decreased as the Fe content increased: ∼9.6 μm in 1-Fe, ∼3.2 μm in 2.5-Fe, and ∼1.5 μm in 4-Fe (Fig. 3). These results indicate that the Fe content affected the phase transformation mechanism.

The phase transformation mechanism was further confirmed by examining the chemical composition of the transformed α phase. A representative result of 4-Fe at two extreme cooling rates, 75 and 0.01 °C/s, is given in Fig. 4. At a cooling rate of 75 °C/s, the chemical composition of the transformed α phase was very similar to that of the retained β phase (Fig. 4a), confirming that the α phase was transformed from β phase via a diffusionless mechanism. In contrast, at a cooling rate of 0.01 °C/s, the two phases showed a large difference in chemical composition (Fig. 4b), verifying the occurrence of a diffusion-based β → α transformation.

The phase transformation temperature decreased as the Fe content increased. Dilatometer results (Fig. 2; Table 2) showed that the difference in Tₐ (ΔTₐ) among the alloys was insignificant at low cooling rates but increased notably as the cooling rate increased. Specifically, ΔTₐ between 1-Fe and 4-Fe was only 30 °C at a cooling rate of 0.1 °C/s, but was 146 °C at a cooling rate of 20 °C/s. These results showed that the Fe content affected the activation of the phase transformation; in particular, the Fe content had a more pronounced effect on diffusionless transformation than on diffusional transformation.

A unique microstructure developed in the 4-Fe sample that had been cooled at a cooling rate of 75 °C/s (Fig. 3c). To examine this microstructure, we compared the EBSD results for 2.5-Fe and 4-Fe, both of which had been cooled at 75 °C/s. 2.5-Fe had a typical martensitic structure along with a small amount of retained β phase (Fig. 5b), as confirmed by the phase map (Fig. 5b). In contrast, 4-Fe appeared to have undergone almost no phase transformation and therefore showed a β-phase microstructure (Fig. 5c). The phase map (Fig. 5d) verified that the β phase was dominant in the microstructure, and martensite formation was limited to the prior β grain boundaries. That is, the β stability was high, especially in 4-Fe due to its relatively high Fe content. Such strong β stability is expected to have significantly affected the overall phase transformation behavior of 4-Fe; this effect will be discussed in Section 4.1.2.

### 3.2. Hardness

The cooling rate also notably affected the hardness of the tested alloys (Fig. 6). The variation in hardness with cooling rate was similar in 1-Fe and 2.5-Fe, but 4-Fe showed two clear differences. First, when the cooling rate increased from 7.5 to 20 °C/s, the hardness increased by 56 Hv in 4-Fe, but by only ∼16 Hv in 1-Fe and 2.5-Fe. Second, as the cooling rate further increased from 20 to 75 °C/s, the hardness decreased in 4-Fe, but not in 1-Fe and 2.5-Fe.

<table>
<thead>
<tr>
<th>Element</th>
<th>Transformed α’ phase (wt.%)</th>
<th>Retained β phase (wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti</td>
<td>90.6</td>
<td>90.2</td>
</tr>
<tr>
<td>Al</td>
<td>5.46</td>
<td>5.67</td>
</tr>
<tr>
<td>Fe</td>
<td>3.96</td>
<td>4.11</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Element</th>
<th>Transformed α phase (wt.%)</th>
<th>Retained β phase (wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti</td>
<td>94.3</td>
<td>77.0</td>
</tr>
<tr>
<td>Al</td>
<td>5.67</td>
<td>3.63</td>
</tr>
<tr>
<td>Fe</td>
<td>0.00</td>
<td>19.3</td>
</tr>
</tbody>
</table>

Fig. 4 – EDS-SEM measurement results showing the chemical composition of transformed α phase and retained β phase in 4-Fe at two extreme cooling rates: (a) 75 °C/s and (b) 0.01 °C/s. The values given are the averages measured over the areas indicated by yellow rectangles.
In all three alloys, the hardness increased when the cooling rate was decreased from 0.1 to 0.01 °C/s (Fig. 6), contradicting the general trend [9] of decreasing hardness with decreasing cooling rate. At a cooling rate of 0.01 °C/s, a coarse lamellar structure was formed in the microstructure of all the alloys (Fig. 3). This structure typically degrades the material strength [22]; therefore, the hardening at a cooling rate of 0.01 °C/s must be a result of some factor(s) other than the microstructure of the alloys that had been cooled at an extremely low cooling rate. This phenomenon will be discussed in Section 4.2.
4. Discussion

4.1. Effect of Fe on phase transformation behavior

4.1.1. Phase transformation mechanism

Our results showed that the Fe content and cooling rate affected the phase transformation mechanisms in the Ti-5Al-xFe alloys. We combined the dilatometer results and microstructural observations to construct phase transformation diagrams for the three alloys (Fig. 7). Comparing these diagrams revealed that the presence of Fe led to a reduction in the critical cooling rate at which only diffusional transformation occurred, thereby shifting the martensite formation region to a lower cooling rate. This suggests that Fe atoms impede long-range diffusional phase transformation and facilitate diffusionless transformation. At room temperature, the solubility of Fe in the α phase is very low (0.047 wt% [23]), implying that precipitation of the equilibrium α phase in these alloys requires significant redistribution of the Fe atoms. The fact that Fe significantly stabilizes the β phase [24] supports the hypothesis that redistribution of the Fe atoms is important in diffusion-based β → α transformations. We observed almost no content of Fe atoms in α phase that had been transformed via the diffusion mechanism (Fig. 4b). This experimental result clearly substantiates the importance of Fe atom redistribution in diffusion-based β → α transformations. Therefore, it can be concluded that an increase in the Fe content impedes the diffusional transformation because of the increased need for Fe atom redistribution.

With increasing Fe content, the thickness of the α plates formed in the lamellar structure decreases (Fig. 3), which is also attributable to the redistribution of Fe atoms. The α plates grow by the movement of the α/β interphase boundaries during the diffusional phase transformation [25], which is concomitant with the ejection of β-stabilizing Fe atoms from the α phase to the β phase across the boundaries. Thus, when the Fe content is increased, the time required to carry the Fe atoms out of the α phase increases; as a result, the interphase boundary movement slows down, thus decreasing the thickness of the α plates.

Redistribution of the Fe atoms also plays an important role in α-phase nucleation. However, the β grain boundaries and pre-formed α/β interphase boundaries, which are preferential nucleation sites [26–28], provide fast diffusion paths for the Fe atoms [16,25]. As a result, nucleation would be less sensitive to Fe content than growth. Thus, an increase in Fe content is likely to induce nucleation-dominant diffusional β → α transformation, thereby leading to the development of a fine lamellar structure. For the same reason, an increase in Fe content decreases the cooling rate at which the Widmanstätten structure is formed (Fig. 7).

4.1.2. Phase transformation start temperature

In the alloys tested, T<sub>s</sub> decreased when the transformation mechanism changed from diffusional to diffusionless (Fig. 7; Table 2). Generally, diffusional transformation occurs in an equilibrium manner, so β → α transformation begins as soon as the temperature decreases below T<sub>α</sub> [1]. In contrast, martensite formation requires sufficient undercooling from T<sub>α</sub> [29], so

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Fig. 7 – Phase transformation diagrams during continuous cooling at various cooling rates: (a) 1-Fe, (b) 2.5-Fe, and (c) 4-Fe. The diagrams were plotted based on dilatometer results and microstructure observations. T<sub>s</sub>, phase transformation start temperature; T<sub>f</sub>, phase transformation finish temperature, i.e., the temperature below which further cooling does not increase the amount of martensite or α phase.
diffusionless phase transformation begins at $T = T_p$ [29]. These facts explain why $T_s$ increases in these alloys as the cooling rate decreases.

$T_s$ was also found to be influenced by the Fe content (Fig. 7). Because Fe is a $\beta$ stabilizer, it causes a decrease in $T_s$ [29]; thus, $T_s$ decreases as the Fe content increases. The difference in $T_p$ ($\Delta T_p$) between 1-Fe and 4-Fe was 67 $^\circ$C, which well accounted for their $\Delta T_s$ at low cooling rates (e.g., $\Delta T_s = 55$ $^\circ$C at a cooling rate of 0.3 $^\circ$C/s). However, their $\Delta T_s$ significantly increased with increasing cooling rate because the corresponding reduction in $T_s$ was significantly larger in 4-Fe than in 1-Fe. The $\Delta T_p$ value could not explain this large $\Delta T_s$. At a cooling rate of 75 $^\circ$C/s, phase transformation was nearly absent in 4-Fe (Fig. 5d), but was almost complete in the other alloys. This result suggests that the effective $T_p$ of 4-Fe decreased at high cooling rates, until it was lower than $T_p$ (923 $^\circ$C), as measured by the simultaneous TGA/DSC analysis (Fig. 1). Accordingly, for 4-Fe, $T_s$ must decrease to the same extent as the effective $T_p$, thereby causing a significant $\Delta T_s$ between 1-Fe and 4-Fe at high cooling rates.

The Fe content can influence $T_s$ by affecting the critical undercooling required for martensite formation [29]. Our results demonstrate that Fe suppresses diffusional transformation, thereby facilitating diffusionless transformation (Fig. 7). Therefore, Fe atoms should reduce the level of undercooling required for martensite formation and thus increase $T_s$ during cooling. However, this effect appeared to be insignificant given that 4-Fe showed a more substantial reduction in $T_s$ at high cooling rates than 1-Fe and 2.5-Fe.

4.1.3. Comparison with Ti-6Al-4V alloy

In the Ti-6Al-4V alloy, the diffusional mechanism dominates the continuous-cooling phase transformation at cooling rates $\leq$410 $^\circ$C/s [6]. However, the present alloys showed diffusional transformation without martensite formation at much lower cooling rates: 7.5 $^\circ$C/s in 1-Fe, 3 $^\circ$C/s in 2.5-Fe, and 1 $^\circ$C/s in 4-Fe. This trend reveals that the Fe atoms suppress long-range diffusional phase transformation and facilitate diffusionless transformation more strongly in Ti-5Al-xFe alloys than V atoms in Ti-6Al-4V. Fe atoms diffuse $\sim$23 times faster in the Ti matrix than V atoms do [30]. Thus, diffusion-based phase transformation should be delayed to a lesser extent in the Ti-5Al-xFe alloys than in Ti-6Al-4V; however, the contrary was observed. V is $\sim$60 times more soluble than Fe in the $\alpha$ phase [31]; therefore, diffusional transformation is much less sensitive to the redistribution of the $\beta$-stabilizing element in Ti-6Al-4V than in the Ti-5Al-xFe alloys. Consequently, diffusional transformation is facilitated to a greater extent in Ti-6Al-4V.

4.2. Factors affecting hardness

The thickness of the $\alpha$ plates in the microstructure is an important factor in determining material hardness [32,33]. Our experimental results showed that Fe content influenced the $\alpha$-phase structure by affecting the transformation mechanism. The thickness of the $\alpha$ plates decreased with increasing Fe content (Fig. 3). This is a major reason why the hardness was observed to be higher as the Fe content increased at a given cooling rate (Fig. 6). We also confirmed that increasing cooling rate decreased the thickness of the $\alpha$ plates (Fig. 3), which in turn increased the hardness of the three alloys (Fig. 6). The variation in hardness with cooling rate was similar in 1-Fe and 2.5-Fe, but 4-Fe showed clear differences (Fig. 6). First, at a cooling rate of 20 $^\circ$C/s, 4-Fe was much harder than 1-Fe and 2.5-Fe compared to the difference in hardness among the samples at lower cooling rates. Second, as the cooling rate increased to 75 $^\circ$C/s, the hardness decreased in 4-Fe, but not in 1-Fe and 2.5-Fe. These observations indicate that the hardness of 4-Fe was influenced by other factor(s) at cooling rates $\geq$ 20 $^\circ$C/s, unlike that of the other alloys.

According to the OM results (Fig. 3), at cooling rates $\leq$ 7.5 $^\circ$C/s, the three alloys showed little difference in the amount of $\beta$ phase in microstructure. However, as cooling rate increased to 20 $^\circ$C/s, the amount of $\beta$ phase was noticeably greater in 4-Fe than in the other alloys. To verify this observation, an EBSD phase map analysis was performed on the microstructures of the 2.5-Fe and 4-Fe samples cooled at 20 $^\circ$C/s. The fraction of $\beta$ phase was clearly higher in 4-Fe (7.3%) than in 2.5-Fe (2.7%) at a cooling rate of 20 $^\circ$C/s (Fig. 8). We also observed that the morphology of this phase was finer in 4-Fe than in 2.5-Fe (Fig. 8). For these two reasons, the number of interphase boundaries between the $\beta$ phase and martensite was substantially higher in 4-Fe than in 2.5-Fe at a cooling rate of 20 $^\circ$C/s. Thus, boundary strengthening (i.e., Hall–Petch hardening) was expected to be much more intense in 4-Fe than in 2.5-Fe. This factor could have been responsible for the remarkably increased hardness of 4-Fe cooled at 20 $^\circ$C/s. In contrast, as the cooling rate increased from 20 to 75 $^\circ$C/s, boundary strengthening was reduced because the near-complete lack of transformation in 4-Fe (Fig. 5c and d) and thus the decreased the number of interphase boundaries.

Fig. 8 – EBSD phase map of the microstructure of 2-Fe and 4-Fe cooled at 20 $^\circ$C/s, showing the area fraction of martensite and retained $\beta$ phase.
Consequently, the hardness of 4-Fe decreased as the cooling rate was increased from 20 to 75 °C/s.

Interestingly, in all three alloys, the hardness was increased at an extremely low cooling rate of 0.01 °C/s despite the presence of coarse lamellar structures in their microstructures (Fig. 3). This result contradicted the trend of material strength decreasing along with the development of a coarse lamellar structure [9]. To identify the reason for this unexpected trend, the microstructure of 2.5-Fe cooled at 0.01 °C/s was analyzed by TEM. The β phase in the lamellar structure had a unique lath-like structure (Fig. 9a), and bracket-like diffraction patterns were seen in addition to the typical β-phase diffraction patterns (Fig. 9b); the same result was observed for 1-Fe and 4-Fe. In contrast, these characteristics were not observed at a cooling rate of 0.1 °C/s (Fig. 9c and d). The formation of the bracket-like diffraction patterns is evidence of the incomplete β → ω decomposition [34]. Generally, in Ti alloys with a lamellar structure, part of the β phase decomposes to ω phase to reduce the free energy of the entire system [34,35] during long-term aging heat treatment [34]. However, at a cooling rate of 0.01 °C/s, the time required for complete β → ω decomposition was insufficient because the alloys were exposed to temperatures of 400–500 °C for less than three hours, which is the range wherein the ω phase can form in Ti alloys [36]. In addition, in the present alloys, the Fe atoms appeared to hinder perfect β → ω decomposition owing to their strong stabilizing ability on the β phase. The high-resolution TEM image of a β phase area showed that some atoms were rearranged, causing a change in the local crystal structure (Fig. 9e, white circles). This observation supports the hypothesis of incomplete β → ω decomposition in the β-phase matrix during cooling at an extremely low cooling rate of 0.01 °C/s. ω-phase formation significantly increases the material strength of Ti alloys [36]; hence, the partial β → ω decomposition may be responsible for the remarkably increased hardness of the tested alloys at this cooling rate. Notably, no precipitates were observed in the microstructure of alloys cooled at 0.01 °C/s (Fig. 9a), which indicates that precipitation strengthening was not a factor in the increase in hardness at this low cooling rate.

5. Summary and conclusions

The effect of Fe content on the β → α phase transformation behavior of Ti-5Al-xFe (x = 1, 2.5, 4) alloys during continuous cooling at various cooling rates was investigated. The variation in hardness with the Fe content and cooling rate was also examined to understand how the transformation mechanism and microstructure affected the material strength of these alloys. The following conclusions were drawn:

1) The presence of Fe delayed long-range diffusional phase transformation, thereby facilitating diffusionless transformation even at a low cooling rate. This is because precipitation of the equilibrium α phase requires significant redistribution of the Fe atoms.

2) Fe reduced $T_s$ by lowering $T_p$. The $\Delta T_s$ value of the alloys well explained the $\Delta T_s$ value at a low cooling rate. However, as the cooling rate increased, $\Delta T_s$ increased notably. The main reason for this trend was that Fe significantly stabilized the β phase; hence, the effective $T_p$ decreased as...
The cooling rate increased, and this reduction intensified with the increase in Fe content. The change in the $\beta \rightarrow \alpha$ phase transformation behavior with Fe content led to the development of different microstructures in the three alloys. An alloy with a higher Fe content tended to form a martensitic structure rather than Widmanstätten and lamellar structures.

Compared to 1-Fe and 2.5-Fe, 4-Fe exhibited a more notable increase in hardness when the cooling rate was increased from 7.5 to 20 °C/s. As the cooling rate was further increased from 20 to 75 °C/s, the hardness decreased in 4-Fe, but not in 1-Fe and 2.5-Fe. This difference in the hardness of 4-Fe was caused by its high $\beta$-phase stability resulting from the relatively high Fe content. The alloys studied herein showed a remarkable increase in hardness at a low cooling rate of 0.01 °C/s, even though they all had coarse lamellar structures in their microstructures. This increase was attributed to incomplete decomposition of the $\beta$ phase to the $\omega$ phase at the extremely low cooling rate of 0.01 °C/s.

The abovementioned results deepen our understanding of the $\beta \rightarrow \alpha$ phase transformation behavior and the related strengthening of the alloys addressed in the study. This is expected to aid the design of appropriate solution-heat treatment processes for the Ti-Al-Fe system.

**Conflicts of interest**

The authors declare no conflicts of interest.

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